ipso-Substitution of a Sulphinyl or Sulphonyl Group Attached to Pyridine Rings and its Application for the Synthesis of Macrocycles

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A sulphinyl or sulphonyl group directly bound to the 2- or 4-position of a pyridine ring was readily displaced by several nucleophiles such as RO^-, RS^-, and CN^- to afford the corresponding *ipso*-substitution products. Similarly, 2-halogeno-6-methylsulphinyl- or -methylsulphonyl-pyridines also react with nucleophiles to afford 2-halogeno-6-substituted pyridine derivatives. Thus, the leaving abilities of the leaving groups fall in the order $RSO_2 > RSO > Br \simeq Cl \gg RS$ (R = alkyl or benzyl). The *ipso*-substitution can be applied to the synthesis of 2,6-disubstituted pyridino macrocycles containing both carbon–oxygen and carbon–sulphur bridges, resulting in several new macrocycles in moderate yields.

Generally, substitution reactions of aromatic compounds with nucleophiles have been classified into the following categories.[1]† (1) Addition–elimination (*ispo*-substitution), (2) elimination–addition (benzene process), (3) S_{RN}-type substitution. These nucleophilic aromatic substitutions have been also observed with heterocyclic compounds such as 2-halogenopyridines.[2] Moreover, nucleophilic substitution on a pyridine ring takes place more readily than on simple benzene systems, since the halogen atom in 2- or 4-halogenopyridines can be substituted readily by several nucleophiles such as amines, alkoxides, and thiolates while the corresponding substitution of simple halogenobenzenes does not take place under the same reaction conditions except for compounds having strong electron-withdrawing substituents such as a nitro group. Recently, we have prepared several sulphur compounds containing a pyridine ring and have shown that alkyl 2-pyridyl sulphoxides or 2,6-disulphinylpyridine derivatives can be used as effective phase-transfer catalysts.[3] However, the general reactivities of these sulphur compounds containing a pyridine ring have not been very well investigated.

During our studies on the physical and chemical properties of organic sulphur compounds containing a pyridine ring, we have found that these compounds undergo several unusual reactions which had not been observed with simple benzene systems. For example, when benzyl or allyl 2-pyridyl sulphoxide was treated with Grignard or organolithium reagents, the intramolecular coupling reaction between the benzyl or allyl group and the 2-pyridyl group took place resulting in 2-benzyl- or 2-allyl-pyridine in excellent yield.[4] This coupling reaction is considered to proceed *via* an initial attack by the Grignard or organolithium reagent on the sulphinyl sulphur atom in the sulphoxide to form an incipient σ-sulphurane from which intramolecular ligand coupling takes place to give rise to the products.‡ Meanwhile, other nucleophiles, such as alkoxides, thiolates, and cyanide ion, were found to displace readily the sulphinyl or sulphonyl group in 2-substituted pyridine derivatives.[5] In particular, Barlin and Brown have reported their kinetic investigations of these unusual *ipso*-substitution reactions of pyridine and related heterocyclic compounds.[6] Furthermore, we found that when 2-halogeno-6-sulphinyl- or 2-halogeno-6-sulphonyl-pyridine derivatives were treated with alkoxides, thiolates, or cyanide ion as nucleophiles, *ipso*-substitution took place at the position bound to the sulphinyl or sulphonyl group and not the position substituted by halogen, whereas the halogen atom was replaced by treating 2-halogeno-6-sulphenylpyridines with the same nucleophiles and the sulphenyl group was not displaced by nucleophiles under the same conditions. We have applied the *ipso*-substitution for the synthesis of a new type of macrocycle containing a pyridine ring. A number of macrocyclic polyethers referred to as 'crown ethers'[7] have been synthesized and their abilities to form complexes with a number of metals have been examined.[8] Meanwhile, hetero-crown compounds such as cyclic polyamines and cyclic polythioethers, and their complexes with metals, have also been studied extensively.[9] Newkome *et al.*,[10] and Vogtle and Webber,[11] have prepared such macrocycles containing a pyridine ring and tested their roles as ligands for complexing with various cations. However, these types of macrocycles, especially carbon–oxygen-bridged 2,6-pyridino-macrocycles in which the bridging oxygens are directly attached to the pyridine ring, were difficult to prepare in good yield.[12] Therefore, we tried the preparation of a new type of 2,6-pyridino macrocycle containing carbon–oxygen and carbon–sulphur bridges in which both oxygen and sulphur atoms are directly attached to the pyridine ring by using the *ipso*-substitution method. This paper describes the results of our endeavours.

Results and Discussion

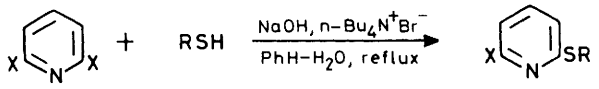
The preparation of sulphinyl or sulphonyl derivatives containing a pyridine ring was carried out by employing the displacement reaction of 2-halogeno- or 2,6-dihalogeno-pyridines with thiolate anion in alcohol.[13] However, when 2,6-dihalogenopyridines were treated with several thiolates under phase-transfer conditions (PTC) using quaternary ammonium salts, *e.g.* tetra-n-butylammonium bromide, and sodium hydroxide as a base in a two-phase system, the reaction stopped at the mono-substitution stage affording solely the 2-halogeno-6-sulphenylpyridine in quantitative yield. The results are summarized in Table 1. These reactions were generally carried out with excess of thiolate but did not proceed with other nucleophiles, *e.g.* RO^-, CN^-, SH^-, and OH^-. These

† Three types of aromatic substitution are reviewed in the following articles. Ar (S_N, Addition–Elimination): J. F. Bunett, *Q. Rev. Chem. Soc.*, 1958, **12**, 1; J. Miller, 'Nucleophilic Aromatic Substitution,' Elsevier, Amsterdam, 1968. Benzyne mechanism: E. K. Field, 'Organic Reactive Intermediates,' Academic Press, New York, 1973, p. 449. S_{RN} Mechanism: J. F. Bunnett, *Acc. Chem. Res.*, 1978, **11**, 413.

‡ σ-Sulphuranes have been reviewed: J. C. Martin and E. F. Perozzi, *Science*, 1976, **191**, 154.

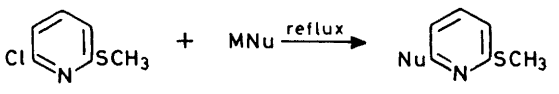
observations reveal that these PTC reactions are promoted by only such strong nucleophiles as thiolates. The mechanism and actual species involved in the reaction are not known well. However, the results suggest that the nucleophiles are well hydrated and hence the reaction may stop at the mono-substitution stage despite the use of excess of thiolate.

Table 1. Reaction of 2,6-dihalogenopyridines with several thiolates



X	R	Time (h)	Product yield (%)	
Cl	CH_3	6	98	(**1**)
Br	CH_3	6	97	(**2**)
Cl	C_2H_5	16	89	(**3**)
Cl	n-C_4H_9	16	82	(**4**)
Br	$C_6H_5CH_2$	11	82	(**5**)

Table 2. Reaction of 2-chloro-6-methylsulphenylpyridine (**1**) with several nucleophiles

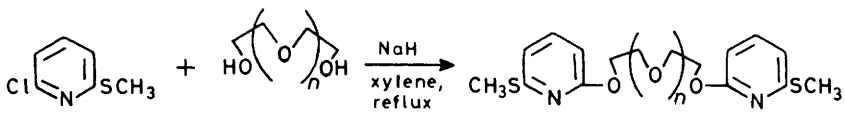


MNu	Solvent	Time (h)	Product yield (%)	
CH_3ONa	CH_3OH	20	100	(**6**)
C_2H_5ONa	C_2H_5OH	13	70	(**7**)
CH_3SNa	C_2H_5OH	11	83	(**8**)
C_2H_5SNa	C_2H_5OH	13	76	(**9**)

When one of these products, 2-chloro-6-methylsulphenylpyridine (**1**), was treated with several nucleophiles such as alkoxides and thiolates in refluxing alcohol, pyridine derivatives bearing two different substituents at the 2- and 6-position, *e.g.* 2-alkoxy-6-methylsulphenyl or 2,6-bis(alkylsulphenyl)pyridines, were obtained in good yields as shown in Table 2. Moreover, the reaction of 2-chloro-6-methylsulphenylpyridine (**1**) with several oligoethylene glycols in the presence of sodium hydride as a base in refluxing xylene afforded oligoether-bridged methylsulphenylpyridines in good yields as shown in Table 3. These bridged products were readily oxidized to the corresponding sulphoxides or sulphones upon treatment with *m*-chloroperbenzoic acid or hydrogen peroxide in *ca.* quantitative yield as shown in Table 4. Oxidation of 2-halogeno-6-alkylsulphenylpyridine derivatives with *m*-chloroperbenzoic acid or hydrogen peroxide also afforded the corresponding sulphoxides or sulphones in good yield. Furthermore, when these sulphoxides or sulphones were treated with alkoxides or thiolates as nucleophiles, *ipso*-substitution took place at the position bound to the sulphinyl or sulphonyl group and not at the position substituted by halogen. When the sulphoxides were used as substrates, the major reaction was *ipso*-substitution at the position bound to the sulphinyl group, but the reduction was also observed to afford the corresponding sulphides as minor products. On the other hand, when sulphones were used as substrates, the reduction was not observed under the same conditions and only the corresponding displacement products by nucleophiles were obtained in good yields. The results of these *ipso*-substitution reactions are summarized in Table 5.

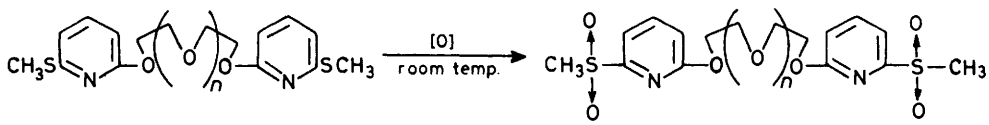
Barlin and Brown have already reported[6] the kinetic results of these *ipso*-substitution reactions of 2-methylsulphinyl- or 2-methylsulphonyl-pyridine with methoxide ion. They also stated that the sulphinyl or sulphonyl group is a better leaving group than chlorine in these *ipso*-substitutions. Therefore, our present observations agree with Barlin's results and indicate

Table 3. Reaction of 2-chloro-6-methylsulphenylpyridine (**1**) with several oligoethylene glycols



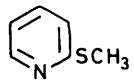
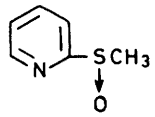
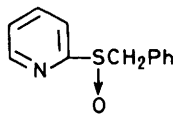
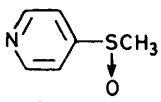
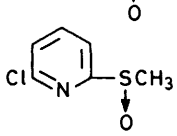
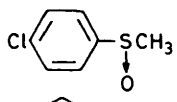
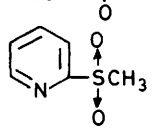
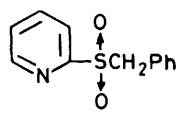
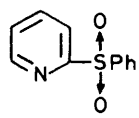
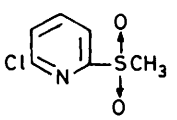
n	Time (h)	Product yield (%)	
0	30	75	(**10**)
1	24	70	(**11**)
2	30	67	(**12**)
3	20	78	(**13**)

Table 4. Oxidation of oligoether-bridged methylsulphenylpyridines



n	[O]	Solvent	Time (h)	Product yield (%)	
0	H_2O_2	AcOH	24	95	(**14**)
1	*m*-CPBA	$CHCl_3$	12	96	(**15**)
1	H_2O_2	AcOH	24	96	(**15**)
2	H_2O_2	AcOH	24	95	(**16**)
3	H_2O_2	AcOH	24	94	(**17**)

Table 5. *ipso*-Substitution reaction of sulphur compounds bound to pyridine with several nucleophiles

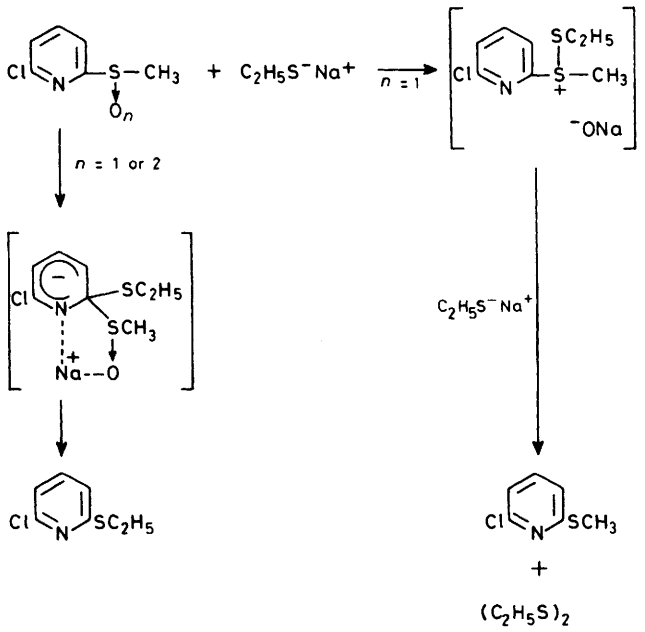
	Substrate	Nucleophile	Solvent	Temp. (C)	Time (h)	Product yields (%) Displacement	Reduction
(18)		C_2H_5ONa	C_2H_5OH	reflux	5	no reaction	
		C_2H_5SNa	C_2H_5OH	reflux	5	no reaction	
(19)		C_2H_5ONa	C_2H_5OH	50	2	73	8
		C_2H_5SNa	C_2H_5OH	50	5	74	18
		PhSK	Bu^{t}OH	reflux	5	47	7
		PhOK	Bu^{t}OH	reflux	18	no reaction	
		C_2H_5ONa	C_2H_5OH	reflux	1.5	80	trace
		C_2H_5ONa	C_2H_5OH	reflux	0.2	16	0 (recovered, 76)
(20)		C_2H_5ONa	C_2H_5OH	reflux	3	63	21
(21)		C_2H_5ONa	C_2H_5OH	50	1	74	13
		C_2H_5SNa	C_2H_5OH	room temp.	1.5	68	20
		C_2H_5ONa	C_2H_5OH	reflux	14	no reaction	
(22)		C_2H_5ONa	C_2H_5OH	reflux	1.5	79	0
		C_2H_5ONa	C_2H_5OH	reflux	0.2	56	
		C_2H_5ONa	C_2H_5OH	reflux	0.2	87	0 ($PhSO_2Na$, 63)[e]
(23)		C_2H_5ONa	C_2H_5OH	50	1	84	0
		C_2H_5SNa	C_2H_5OH	room temp.	1.5	90	0
		C_2H_5SNa[a]	Benzene	reflux	0.25	100	0
		C_2H_5SH–Et_3N	C_2H_5OH	reflux	75	26	0 (recovered, 56)
		NaCN	DMF[b]	room temp.	162	94[c]	0
		NaCN	DMF	60	12	76[d]	0

[a] In the presence of 18-crown-6. [b] Dimethylformamide. [c] 2-Chloro-6-cyanopyridine, m.p. 85—88 °C [lit. (H. Tani, *Chem. Pharm. Bull.*, 1959, **7**, 930) 86—88 °C]. [d] Generally the reaction was carried out under N_2. However, in the O_2 atmosphere or degassed conditions or in the dark, the substitution reaction proceeded to afford the substitution product in almost the same yield as the standard conditions. [e] Sodium benzenesulphinate was identified by comparison of the i.r. and n.m.r. spectra with those of an authentic sample.

that the leaving ability of the leaving groups in these *ipso*-substitution reactions of pyridines falls in the order $RSO_2 > RSO > Br \gtrsim Cl \gg RS$,[13] whereas the attacking ability of the nucleophiles seems to follow the order $RS^- > RO^- > {}^-CN$. Although the mechanism of the reaction is not known, these observations suggest that both the *ipso*-substitution and the reduction would proceed *via* the paths shown in Scheme 1.

Initially, 2-chloro-6-methylsulphinylpyridine (**21**) reacts with thiolate anion at two different reaction sites, namely, either at the α-carbon atom in the pyridine ring or at the sulphinyl sulphur atom. In the first reaction, the nucleophile attacks the α-position of the pyridine ring, *i.e.* simple *ipso*-substitution. On the other hand, in the second reaction occurring at the sulphur atom, the nucleophile attacks the sulphinyl sulphur atom to afford initially the sulphonium-type intermediate which undergoes reduction to yield the reduced product.* On the other hand again, 2-chloro-6-methylsulphonylpyridine (**23**) reacts with the thiolate anion only at the carbon bearing the sulphonyl group in the pyridine ring affording the corresponding *ipso*-substituted product. Thus, the sulphonyl group serves as a better leaving group for introducing nucleophiles in the

* Thiolate ion has been assumed to reduce sulphoxide to sulphide: see reference 6*b* and J. F. Bunnett, E. W. Garbisch, Jr., and K. M. Pruitt, *J. Am. Chem. Soc.*, 1957, **79**, 355. Leaving ability in nucleophilic aromatic substitutions is discussed in H. Suhr, *Chem. Ber.*, 1964, **97**, 3268.



Scheme 1.

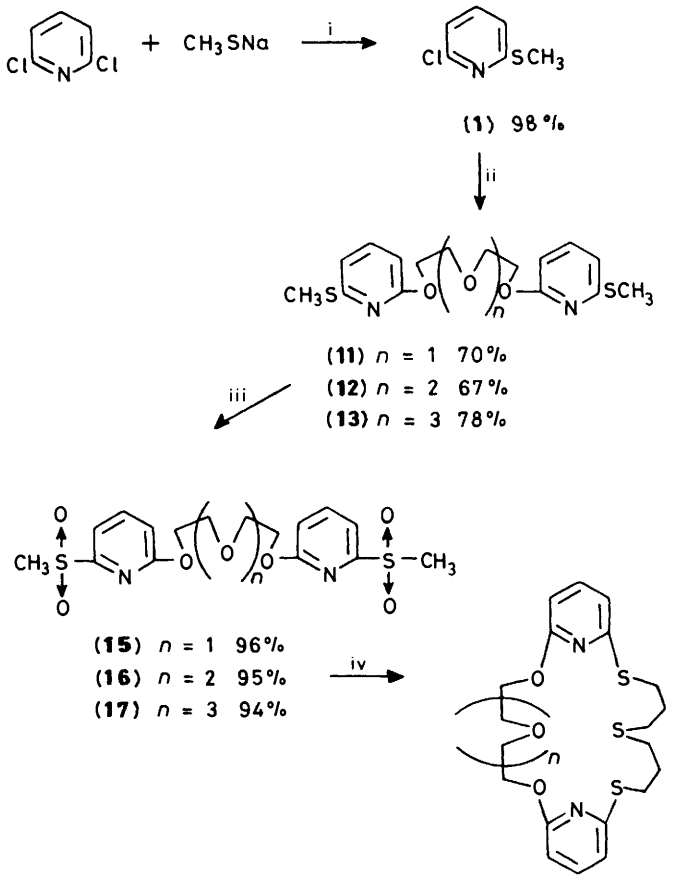
pyridine ring than does the sulphinyl group. By using these sequential *ipso*-substitution reactions in the pyridine ring, one can obtain 2,6-disubstituted pyridine derivatives bearing different kinds of oxygen and sulphur substituents.

Similarly, when 2-chloro-6-methylsulphonylpyridine (**23**) was treated with NaCN in DMF at room temperature for a week or at 60 °C for 12 h it afforded 2-chloro-6-cyanopyridine in 94 and 76% yield respectively. However, when this reaction was carried out at higher temperature, *e.g.* refluxing DMF, 2,6-dicyanopyridine was the major product. The results are also shown in Table 5. Furthermore, the reaction of 2-chloro-6-methylsulphonylpyridine with NaCN in DMF proceeded even in the presence of O_2 or under a N_2 stream, or even in the dark to afford 2-chloro-6-cyanopyridine in good yield. These results suggest that the mechanism for the reaction should proceed *via* an ionic path and not involve a radical process; however, more detailed investigation is required to clarify this point.

This *ipso*-substitution in the pyridine ring has been applied further for the synthesis of new types of 2,6-disubstituted macrocycles containing both carbon–oxygen and carbon–sulphur bridges. The synthesis of 2,6-pyridinomacrocycles in which the bridging oxygen and sulphur are directly attached to the pyridine ring was carried out as shown in Scheme 2, starting with 2,6-dichloropyridine and proceeding *via* the formation of the corresponding oligoether-bridged pyridylsulphone.

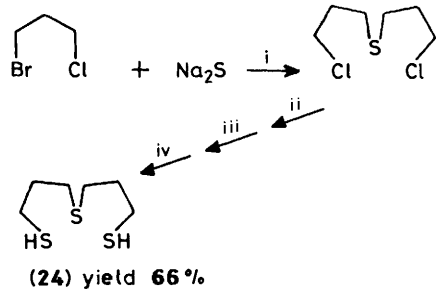
The reaction of 2,6-dichloropyridine with sodium methyl*thio*late under the usual PTC conditions afforded 2-chloro-6-methylsulphenylpyridine (**1**) in 98% yield. Treatment of this sulphide (**1**) with oligoethylene glycol dianions in refluxing xylene afforded the corresponding oligoether-bridged methylsulphenylpyridines (**10**)—(**13**) in moderate yields as shown in Table 3. These sulphides were readily oxidized to the corresponding sulphones (**14**)—(**17**) in quantitative yields as shown in Table 4. Then, we tried to prepare several macrocycles containing two pyridine rings which are directly substituted by both oxa- and thia-bridges, using these *ipso*-substitutions. Thus, 4-thiapentane-1,7-dithiol (**24**), prepared by the procedure shown in Scheme 3, was used as the nucleophile.

Treatment of oligoether-bridged sulphonylpyridines with the dithiolate in refluxing t-butyl alcohol afforded 1:1 cyclized macrocycles (**A**)—(**C**) in relatively good yields. The products



Total yield	Cyclization reaction yield
(**A**) 20%	(**A**) *n* = 1 31%
(**B**) 21%	(**B**) *n* = 2 34%
(**C**) 19%	(**C**) *n* = 3 26%

Scheme 2. *Reagents and conditions:* i, $Bu^n_4N^+Br^-$, benzene–water, reflux, 6 h; ii, $NaOHCH_2(CH_2OCH_2)_nCH_2ONa$, reflux, 20—30 h; iii, H_2O_2–AcOH, room temp., 24 h; iv, $KS[CH_2]_3S[CH_2]_3SK$, reflux, then dilution, 10 h



Scheme 3. *Reagents:* i, Aqueous ethanol; ii, $(NH_2)_2C{=}S$, ethanol; iii, aqueous KOH; iv, H_2SO_4

thus obtained were purified by column chromatography and the structures of these compounds were determined by n.m.r., i.r., and mass spectrometry, and elemental analyses. High-dilution techniques were utilized in an attempt to increase the yields of the cyclized products. Generally, 1:1 cyclizations predominate over 2:2 or 3:3 cyclizations under these dilution conditions. Therefore, these stepwise syntheses of macrocycles have the following advantages. (1) Moderate yields: the yields

for the cyclization to (A)—(C) were 31, 34, and 26% respectively. The total yields of the macrocycles (A)—(C) were 20, 21, and 19% respectively. (2) The number of oxygen and sulphur atoms in the macrocyclic ring can be controlled freely or systematically by changing the glycol oligomers or thioether derivatives in the present investigation and also the ring size can be freely changed. (3) As shown above, three different bridged macrocycles which are otherwise difficult to prepare can be synthesized quite readily by the present process. Thus, the new macrocycles containing a pyridine ring have been obtained in good yields by these simple procedures *via ipso*-substitution.

Experimental

General.—All m.p.s were uncorrected and were taken on a Yanako micro melting-point apparatus. I.r. spectra were obtained on a JASCO A-3 spectrophotometer and n.m.r. spectra were obtained on a Hitachi R-600 FT-NMR spectrometer or a JEOL LNM-MH-100 spectrometer in $CDCl_3$ or CCl_4 using $SiMe_4$ as internal standard. All the reactions were monitored by chromatography, namely t.l.c. (Merck Kieselgel 60-GF_{254}), g.l.p.c. [Hitachi 163, using a 5% silicone GE SE-30 on SiO_2 (60—80 mesh) or 2% silicone OV-1 Chromosorb W on SiO_2 (80—100 mesh) column], l.l.c. (JAI LC-09 or Jasco Familic-100N). Silica gel used for column chromatography was Merck Kieselgel 60. Mass spectra were taken with a Hitachi RMU-6MG mass spectrometer. Elemental analyses were carried out by the Chemical Analysis Center in this University.

Materials.—All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Reactions of 2,6-*Dichloropyridine with Thiolates.*—A typical experimental procedure is as follows. To a solution of 2,6-dichloropyridine (50 g, 0.338 mol) and the sodium salt of methanethiol (15% aqueous solution; 237 g, 0.507 mol) in benzene (150 ml) was added tetra-n-butylammonium bromide (3 g, 9.3 mmol) and the heterogeneous solution was vigorously stirred and refluxed for 6 h. After separation of the organic layer, the organic layer was washed with water and dried (anhydrous $MgSO_4$). After the solution had been filtered and evaporated to dryness, the residue was distilled under reduced pressure to afford a liquid which was identified as 2-*chloro*-6-*methylsulphenylpyridine* (**1**), yield 98%, b.p. 105—107 °C at 14 mmHg; $\nu_{max.}$(neat) 2 940, 1 570, 1 415, 1 160, and 795 cm^{-1}; $\delta(CCl_4)$ 2.47 (3 H, s, CH_3) and 6.60—7.37 (3 H, m, pyrH) (Found: C, 45.2; H, 3.8; N, 9.0. C_6H_6ClNS requires C, 45.1; H, 3.8; N, 8.8%). The following compounds were similarly prepared.

2-*Bromo*-6-*methylsulphenylpyridine* (**2**), yield 97%, b.p. 128—132 °C at 16 mmHg; $\nu_{max.}$(neat) 2 920, 1 560, 1 405, 1 155, and 770 cm^{-1}; $\delta(CDCl_3)$ 2.50 (3 H, s, CH_3) and 6.78—7.53 (3 H, m, pyrH) (Found: C, 35.7; H, 2.9; N, 6.95. C_6H_6BrNS requires C, 35.3; H, 3.0; N, 6.95%).

2-*Chloro*-6-*ethylsulphenylpyridine* (**3**), yield 89%, b.p. 130.5—136.0 °C at 23 mmHg; $\nu_{max.}$(neat) 2 930, 1 570, 1 450, 1 160, and 890 cm^{-1}; δ (CCl_4) 1.36 (3 H, t, *J* 8 Hz, CH_3), 3.14 (2 H, q, *J* 8 Hz, CH_2), and 6.75—7.40 (3 H, m, pyrH) (Found: C, 48.45; H, 4.7; N, 8.0. C_7H_8ClNS requires C, 48.4; H, 4.6; N, 8.1%).

2-*n*-*Butylsulphenyl*-6-*chloropyridine* (**4**), yield 82%, b.p. 155—159 °C at 25 mmHg; $\nu_{max.}$ (neat) 2 960, 1 570, 1 410, 1 160, and 790 cm^{-1}; $\delta(CCl_4)$ 0.82—1.89 (7 H, m, $CH_2CH_2CH_3$), 3.11 (2 H, t, *J* 8 Hz, CH_2S), and 6.73—7.39 (3 H, m, pyrH) (Found: C, 53.65; H, 6.1; N, 6.8. $C_9H_{12}ClNS$ requires C, 53.6; H, 6.0; N, 6.9%).

2-Benzylsulphenyl-6-bromopyridine (**5**), yield 82%, b.p. 164—167 °C at 3 mmHg; $\nu_{max.}$(neat) 3 040, 1 565, 1 410, 1 160, and 770 cm^{-1}; $\delta(CCl_4)$ 4.25 (2 H, s, CH_2S) and 6.70—7.73 (8 H, m, pyrH and Ph).

Reactions of 2-*Chloro*-6-*methylsulphenylpyridine* (**1**) *with Nucleophiles.*—A typical experimental procedure is as follows. To a solution of sodium metal (130 mg, 5.65 mg-atom) in ethanol (4 ml) was added dropwise 2-chloro-6-methylsulphenylpyridine (**1**) (200 mg, 1.25 mmol) under nitrogen. After the mixture had been refluxed for 13 h, the solvent was removed under reduced pressure. The residue was treated with water and extracted with dichloromethane (3 × 30 ml). The combined extracts were dried (anhydrous $MgSO_4$) and evaporated. The residue was distilled under reduced pressure to afford a liquid (148 mg) which was identified as 2-ethoxy-6-methylsulphenylpyridine (**7**), yield 70%, b.p. 118—124 °C at 26 mmHg (Kugelrohr); $\nu_{max.}$(neat) 2 980, 1 565, 1 435, 1 290, and 785 cm^{-1}: $\delta(CCl_4)$ 1.49 (3 H, t, *J* 8 Hz, CCH_3), 2.60 (3 H, s, SCH_3), 4.45 (2 H, q, *J* 8 Hz, CH_2), 6.33 (1 H, d, *J* 8 Hz, β-pyrH), 6.69 (1 H, d, *J* 8 Hz, β-pyrH), and 7.34 (1 H, t, *J* 8 Hz, γ-pyrH). The following compounds were similarly prepared.

2-Methoxy-6-methylsulphenylpyridine (**6**), yield quantitative, $\delta(CDCl_3)$ 2.71 (3 H, s, SCH_3), 4.10 (3 H, s, OCH_3), and 6.39—7.68 (3 H, m, pyrH).

2,6-*Bis*(*methylsulphenyl*)*pyridine* (**8**), yield 83%, b.p. 95 °C at 3 mmHg; $\nu_{max.}$(neat) 2 925, 1 550, 1 410, 1 140, and 775 cm^{-1}; $\delta(CCl_4)$ 2.28 (6 H, s, CH_3) and 7.14—7.79 (3 H, m, pyrH) (Found: C, 49.3; H, 5.2; N, 8.4. $C_7H_9NS_2$ requires C, 49.1; H, 5.3; N, 8.2%).

2-*Ethylsulphenyl*-6-*methylsulphenylpyridine* (**9**), yield 76%, b.p. 104—108 °C at 5 mmHg (Kugelrohr); $\nu_{max.}$(neat) 2 930, 1 550, 1 410, 1 155, and 775 cm^{-1}; $\delta(CCl_4)$ 1.59 (2 H, t, *J* 8 Hz, CCH_3), 2.74 (3 H, s, SCH_3), 3.35 (2 H, q, *J* 8 Hz, CH_2), and 6.80—7.45 (3 H, m, pyrH) (Found: C, 51.7; H, 6.0; N, 7.7. $C_8H_{11}NS_2$ requires C, 51.85; H, 6.0; N, 7.55%).

Reaction of 2-*Chloro*-6-*methylsulphenylpyridine* (**1**) *with Oligoethylene Glycols.*—A typical experimental procedure is as follows. To a suspension of sodium hydride (*ca.* 50%; 3.36 g, 0.07 mol) in anhydrous xylene (50 ml) under nitrogen was added dropwise diethylene glycol (3.18 g, 0.03 mol). The mixture was stirred for 30 min, then 2-chloro-6-methylsulphenylpyridine (**1**) (10 g, 0.063 mol) was added. The mixture was refluxed for 24 h and the solvent was removed under reduced pressure. The residue was carefully treated with crushed ice, extracted with dichloromethane, and the extract was dried (anhydrous $MgSO_4$) and concentrated. The residue was subjected to column chromatography with n-hexane–ethyl acetate (5:1) as eluant to a pale yellow liquid (7.40 g), identified as 6,6′-*bis*(*methylsulphenyl*)-2,2′-[*oxybis*(*ethyleneoxy*)]*dipyridine* (**11**), yield 70%, $\nu_{max.}$(neat) 2 590, 1 585, 1 435, 1 290, 1 165, 960, and 760 cm^{-1}; $\delta(CDCl_3)$ 2.52 (6 H, s, CH_3), 3.88 (4 H, t, *J* 5 Hz, β-CH_2O), 4.54 (4 H, t, *J* 5 Hz, α-CH_2O), 6.44 (2 H, d, *J* 8 Hz, β-pyrH), and 7.83 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 54.3; H, 5.7; N, 7.9. $C_{16}H_{20}N_2O_3S_2$ requires C, 54.5; H, 5.7; N, 7.9%). The following compounds were similarly prepared.

2,2′-*Ethylenedioxy*-6,6′-*bis*(*methylsulphenyl*)*dipyridine* (**10**), yield 75%, m.p. 94.0—94.5 °C; $\nu_{max.}$(KBr) 2 975, 1 580, 1 415, 1 155, 1 041, 900, and 780 cm^{-1}; $\delta(CDCl_3)$ 2.53 (6 H, s, CH_3), 4.71 (4 H, s, CH_2), 6.46 (2 H, d, *J* 8 Hz, β-pyrH), 6.77 (2 H, d, *J* 8 Hz, β-pyrH), and 7.40 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 54.7; H, 5.3; N, 9.0. $C_{14}H_{16}N_2O_2S_2$ requires C, 54.5; H, 5.2; N, 9.1%).

2,2′-[*Ethylenedioxybis*(*ethyleneoxy*)]-6,6′-*bis*(*methylsulphenyl*)*dipyridine* (**12**), yield 67%, $\nu_{max.}$(neat) 2 950, 1 740, 1 585, 1 445, 1 290, 1 165, 1 055, 790, and 760 cm^{-1}; $\delta(CDCl_3)$ 2.52 (6 H, s, CH_3), 3.73 (4 H, s, γ-CH_2O), 3.84 (4 H, t, *J* 5 Hz, β-CH_2O), 4.52 (4 H, t, *J* 5 Hz, α-CH_2O), 6.44 (2 H, d, *J* 8 Hz, β-pyrH), 6.75 (2 H, *J* 8 Hz, β-pyrH), and 7.38 (2 H, t, *J* 8 Hz, γ-pyrH) (Found:

C, 54.4; H, 6.0; N, 7.1. $C_{18}H_{24}N_2O_4S_2$ requires C, 54.5; H, 6.1; N, 7.1%).

6,6′-*Bis*(*methylsulphenyl*)-2,2′-[*oxybis*(*ethyleneoxyethyleneoxy*)]*dipyridine* (**13**), yield 78%, $\nu_{max.}$(neat) 2 950, 1 735, 1 430, 1 290, 1 160, 790, and 730 cm^{-1}; δ($CDCl_3$) 2.52 (6 H, s, CH_3), 3.69 (8 H, s, γ- and δ-CH_2O), 3.83 (4 H, t, *J* 5 Hz, β-CH_2O), 4.52 (4 H, t, *J* 5 Hz, α-CH_2O), 6.45 (2 H, d, *J* 8 Hz, β-pyrH), 6.75 (2 H, d, *J* 8 Hz, β-pyrH), 7.38 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 54.55; H, 6.5; N, 6.2. $C_{20}H_{28}N_2O_3S_2$ requires C, 54.5; H, 6.4; N, 6.35%).

Oxidation of Oligoether-bridged Sulphenylpyridines.—A typical experimental procedure is as follows. To a solution of 6,6′-bis(methylsulphenyl)-2,2′-[oxybis(ethyleneoxy)]dipyridine (**11**) (1.0 g, 2.84 mmol) in acetic acid (20 ml) was added dropwise 30% hydrogen peroxide (1.6 g, 14.1 mmol). After the mixture had been stirred for 24 h, the solvent was removed under reduced pressure. The residue was dissolved in water and neutralized with dry NH_3 gas, and then extracted with chloroform (3 × 50 ml). The extract was dried (anhydrous $MgSO_4$) and evaporated. The crude product was recrystallized from n-hexane and benzene to afford white crystals (1.14 g) which were identified as 6,6′-*bis*(*methylsulphonyl*)-2,2′-[*oxybis*(*ethyleneoxy*)]*dipyridine* (**15**), yield 96%, m.p. 101—102 °C; $\nu_{max.}$(KBr) 2 950, 2 900, 1 600, 1 440, 1 310 (SO_2), 1 130 (SO_2), 950, 770, and 540 cm^{-1}; δ($CDCl_3$) 3.19 (6 H, s, CH_3), 3.96 (4 H, t, *J* 5 Hz, β-CH_2O), 4.60 (4 H, t, *J* 5 Hz, α-CH_2O), 7.06 (2 H, d, *J* 8 Hz, β-pyrH), 7.70 (2 H, d, *J* 8 Hz, β-pyrH), and 7.87 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 46.2; H, 4.8; N, 6.7. $C_{16}H_{20}N_2O_7S_2$ requires C, 46.1; H, 4.8; N, 6.7%). The following compounds were similarly prepared.

2,2′-*Ethylenedioxy*-6,6′-*bis*(*methylsulphonyl*)*dipyridine* (**14**), yield 95%, m.p. 209—210 °C. $\nu_{max.}$(KBr) 3 020, 1 595, 1 305 (SO_2), 1 120 (SO_2), 1 040, 970, 770, and 540 cm^{-1}; δ ($CDCl_3$) 3.19 (6 H, s, CH_3), 4.77 (4 H, s, CH_2), 6.97—7.12 (4 H, m, β-pyrH), and 7.72—7.78 (2 H, m, γ-pyrH) (Found: C, 45.3; H, 4.3; N, 7.4. $C_{14}H_{16}N_2O_6S_2$ requires C, 45.15; H, 4.3; N, 7.5%).

2,2′-[*Ethylenedioxybis*(*ethyleneoxy*)]-6,6′-*bis*(*methylsulphonyl*)*dipyridine* (**16**), yield 95%, m.p. 132.0—132.5 °C; $\nu_{max.}$(KBr) 2 910, 1 590, 1 440, 1 300 (SO_2), 1 130 (SO_2), 1 035, 970, 765, and 540 cm^{-1}; δ($CDCl_3$) 3.17 (6 H, s, CH_3), 3.73 (4 H, s, γ-CH_2O), 3.86 (4 H, t, *J* 5 Hz, β-CH_2O), 4.55 (4 H, t, *J* 5 Hz, α-CH_2O), 7.02 (2 H, d, *J* 8 Hz, β-pyrH), 7.65 (2 H, d, *J* 8 Hz, β-pyrH), and 7.83 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 47.2; H, 5.2; N, 6.0. $C_{18}H_{24}N_2O_8S_2$ requires C, 46.9; H, 5.25; N, 6.1%).

6,6′-*Bis*(*methylsulphonyl*)-2,2′-[*oxybis*(*ethyleneoxyethyleneoxy*)]*dipyridine* (**17**), yield 94%, m.p. 70—71 °C; $\nu_{max.}$(KBr) 2 925, 2 875, 1 590, 1 420, 1 305 (SO_2), 1 120 (SO_2), 970, 755, and 535 cm^{-1}; δ($CDCl_3$) 3.18 (6 H, s, CH_3), 3.69 (8 H, s, γ- and δ-CH_2O), 3.86 (4 H, t, *J* 5 Hz, β-CH_2O), 4.55 (4 H, d, *J* 5 Hz, α-CH_2O), 7.03 (2 H, d, *J* 8 Hz, β-pyrH), 7.66 (2 H, d, *J* 8 Hz, β-pyrH), and 7.84 (2 H, t, *J* 8 Hz, γ-pyrH) (Found: C, 47.4; H, 5.6; N, 5.5. $C_{20}H_{28}N_2O_9S_2$ requires C, 47.6; H, 5.6; N, 5.55%).

ipso-*Substitution of Pyridine Derivatives with Nucleophilic Substrates.*—*Methyl 2-pyridyl sulphide* (*2-methylsulphenylpyridine*) (**18**). The title sulphide was prepared from 2-mercaptopyridine with iodomethane, according to the general method.[3a] Yield 74%, b.p. 60 °C at 4 mmHg; $\nu_{max.}$(neat) 2 930, 1 580, 1 415, 1 125, and 755 cm^{-1}; δ($CDCl_3$) 2.60 (3 H, s, CH_3), 6.84—7.62 (3 H, m, β-, β-, and γ-pyrH), and 8.39—8.49 (1 H, m, α-pyrH).

Methyl 2-pyridyl sulphoxide (*2-methylsulphinylpyridine*) (**19**), *methyl 4-pyridyl sulphoxide* (*4-methylsulphinylpyridine*) (**20**), *and 2-chloro-6-methylsulphinylpyridine* (**21**). The title sulphoxides were prepared from the corresponding sulphides with *m*-chloroperbenzoic acid or hydrogen peroxide as oxidant according to the general methods.[15]

Sulphoxide (**19**): yield 88%, b.p. 95—96 °C at 1.5 mmHg; $\nu_{max.}$(neat) 3 050, 1 570, 1 420, 1 050 (SO), and 775 cm^{-1}; δ($CDCl_3$) 2.83 (3 H, s, CH_3), 7.20—7.50 (1 H, m, γ-pyrH), 7.74—8.16 (2 H, m, β-pyrH), and 8.32—8.58 (1 H, m, α-pyrH).

Sulphoxide (**20**): yield 49%, b.p. 121—124 °C at 3 mmHg; $\nu_{max.}$(neat) 3 050, 1 660, 1 390, 1 035 (SO), 795, and 500 cm^{-1}; δ($CDCl_3$) 2.74 (3 H, s, CH_3), 7.35 (2 H, d, *J* 6 Hz, β-pyrH), and 8.36 (2 H, d, *J* 6 Hz, α-pyrH).

Sulphoxide (**21**): yield 95%, m.p. 66.0—66.5 °C; $\nu_{max.}$(KBr) 3 080, 1 555, 1 410, 1 120, 1 051 (SO), 810, and 775 cm^{-1}; δ($CDCl_3$) 2.74 (3 H, s, CH_3) and 7.11—7.80 (3 H, m, pyrH) (Found: C, 41.0; H, 3.45; N, 8.0. C_6H_6ClNOS requires C, 41.0; H, 3.4; N, 8.0%).

Methyl 2-pyridyl sulphone (*2-methylsulphonylpyridine*) (**22**) *and 2-chloro-6-methylsulphonylpyridine* (**23**). The title sulphones were prepared from the corresponding sulphides with hydrogen peroxide as oxidant, according to the general methods.[16]

Sulphone (**22**): yield 93%, b.p. 136 °C at 5 mmHg; $\nu_{max.}$(neat) 2 940, 1 580, 1 430, 1 305 (SO_2), 1 165 (SO_2), 1 115, 960, and 765 cm^{-1}; δ($CDCl_3$) 3.18 (3 H, s, CH_3) and 7.24—8.55 (4 H, m, pyrH).

Sulphone (**23**): yield 93%, m.p. 108.5—109.0 °C; $\nu_{max.}$(KBr) 3 030, 2 940, 1 570, 1 420, 1 310 (SO_2), 1 150 (SO_2), 965, 800, and 750 cm^{-1}; δ($CDCl_3$) 3.25 (3 H, s, CH_3), and 7.34—8.04 (3 H, m, pyrH) (Found: C, 37.65; H, 3.1; N, 7.3. $C_6H_6ClNO_2S$ requires C, 37.6; H, 3.15; N, 7.3%).

ipso-*Substitution of the sulphides, sulphoxides, and sulphones.* The reactions were carried out in a two-necked reactor equipped with a condenser. To a mixture of substrate (*e.g.* sulphide, sulphoxide, or sulphone, 200 mg) and a nucleophile (*e.g.* C_2H_5ONa, C_2H_5SNa, PhOK, PhSK, or NaCN, 2 equiv.) was added an alcohol (3 ml) (*e.g.* ethanol, or t-butyl alcohol) or DMF (3 ml). The mixture was stirred at a given temperature under N_2. In the case of CN^- anion, both N_2 and O_2 atomospheres were used for the reaction. Small samples of the reaction mixture were withdrawn by a microsyringe at appropriate time intervals and monitored by gas chromatography. When the reaction was finished, the solvent was removed under reduced pressure. The residue was treated with water and extracted three times with chloroform. The extracts were then evaporated under reduced pressure. The yields of the displacement and the reduction products were determined by n.m.r. analyses.

Synthesis of 4-*Thiaheptane*-1,7-*dithiol* (**24**).—To a solution of 1-bromo-3-chloropropane (20 g, 0.127 mol) in ethanol (110 ml) was added a mixture of sodium sulphide (18.3 g, 0.076 mol) and water (40 ml). After the reaction mixture had been refluxed for 5 h, the solvent was removed under reduced pressure. To a solution of the residue in ethanol (100 ml) was added thiourea (11.6 g, 0.152 mol) and the mixture was refluxed for 24 h. After concentration of the solution, potassium hydroxide (42 g, 0.599 mol) in water (150 ml) was added to the residue. The mixture was refluxed for 5 h under N_2. The mixture was cooled in an ice–water bath and cooled aqueous sulphuric acid was added dropwise until the mixture became acidic. After the addition of acid, the reaction mixture was extracted with chloroform (3 ×) and the extracts were dried (anhydrous $MgSO_4$). After removal of the solvent, the residue was distilled *in vacuo* to afford the known[17] dithiol (**24**) as a liquid (7.7 g, 66%), b.p. 110.0—110.5 °C at 2.5 mmHg; $\nu_{max.}$(neat) 2 930, 2 550 (SH), 1 430, and 1 250 cm^{-1}; δ($CDCl_3$) 1.38 (2 H, t, *J* 8 Hz, SH), 1.92 (4 H, q, *J* 8 Hz, CCH_2C), and 2.41—2.93 (8 H, m, CH_2S).

Synthesis of Macrocycle (**A**).—To a solution of potassium t-butoxide (605 mg, 5.4 mmol) in t-butyl alcohol (35 ml) was added 4-thiaheptane-1,7-dithiol (**24**) (328 mg, 1.8 mmol) under N_2. The mixture was stirred for 15 min at room temperature, then 6,6′-bis(methylsulphonyl)-2,2′-[oxybis(ethyleneoxy)]dipyridine (**15**) (750 mg, 1.8 mmol) was added. After

the reaction mixture had been refluxed for 10 h under N_2, the solvent was removed under reduced pressure. The residue was dissolved in water, extracted with chloroform (3 × 50 ml), and dried (anhydrous $MgSO_4$). After removal of the solvent, the residue was subjected to silica-gel column chromatography with n-hexane–ethyl acetate (3:1) as eluant to afford white crystals of the title macrocycle (244 mg, 31%), m.p. 86—87 °C; $\nu_{max.}$(KBr) 2 890, 1 565, 1 430, 1 290, 1 145, and 790 cm^{-1}; δ($CDCl_3$) 2.03 (4 H, quint, *J* 8 Hz, CCH_2C), 2.67 (4 H, t, *J* 8 Hz, CH_2SCH_2), 3.22 (4 H, t, *J* 8 Hz, CH_2Spyr), 3.90 (4 H, t, *J* 6 Hz, β-CH_2O), 4.58 (4 H, t, *J* 6 Hz, α-CH_2O), 6.44 (2 H, d, *J* 8 Hz, β-pyrH), 6.79 (2 H, d, *J* 8 Hz, β-pyrH), and 7.38 (2 H, t, *J* 8 Hz, γ-pyrH); *m/z*, M^+ 438 (Found: C, 54.6; H, 6.1; N, 6.1. $C_{20}H_{26}N_2O_3S_3$ requires C, 54.8; H, 6.0; N, 6.4%).

Synthesis of Macrocycle (**B**).—To a solution of potassium t-butoxide (548 mg, 4.88 mmol) in t-butyl alcohol (40 ml) was added 4-thiaheptane-1,7-dithiol (297 mg, 1.63 mmol) under N_2. The mixture was stirred for 15 min at room temperature, then 2,2′-[ethylenedioxybis(ethyleneoxy)]-6,6′-bis(methylsulphonyl)dipyridine (**16**) (750 mg, 1.63 mmol) was added. After the reaction mixture had been refluxed for 10 h under N_2, the solvent was removed under reduced pressure. The residue was dissolved in water, extracted with chloroform (3 × 50 ml), and the extracts dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to silica-gel column chromatography with n-hexane–ethyl acetate (5:2) as eluant to afford white crystals of the title macrocycle (266 mg, 34%), m.p. 66—67 °C; $\nu_{max.}$(KBr) 2 900, 1 565, 1 430, 1 290, 1 155, and 790 cm^{-1}; δ($CDCl_3$) 1.99 (4 H, quint, *J* 8 Hz, CCH_2C), 2.64 (4 H, t, *J* 8 Hz, CH_2SCH_2), 3.23 (4 H, t, *J* 8 Hz, CH_2Spyr), 3.71 (4 H, s, γ-CH_2O), 3.84 (4 H, t, *J* 6 Hz, β-CH_2O), 4.51 (4 H, t, *J* 6 Hz, α-CH_2O), 6.43 (2 H, d, *J* 8 Hz, β-pyrH), 6.76 (2 H, d, *J* 8 Hz, β-pyrH), and 7.36 (2 H, t, *J* 8 Hz, γ-pyrH); *m/z*, M^+ 482 (Found: C, 54.6; H, 6.3; N, 5.7. $C_{22}H_{30}N_2O_4S_3$ requires C, 54.7; H, 6.3; N, 5.8%).

Synthesis of Macrocycle (**C**).—To a solution of potassium t-butoxide (500 mg, 4.46 mmol) in 35 ml t-butyl alcohol (35 ml) was added 4-thiaheptane-1,7-dithiol (271 mg, 1.49 mmol) under N_2. The mixture was stirred for 15 min at room temperature, then 6,6′-bis(methylsulphonyl)-2,2′-[oxybis(ethyleneoxyethyleneoxy)] *dipyridine* (**17**) (750 mg, 1.49 mmol) was added. After the reaction mixture had been refluxed for 10 h under N_2, the solvent was removed under reduced pressure. The residue was dissolved in water, extracted with chloroform (3 × 50 ml), and the extracts dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to silica-gel column chromatography with n-hexane–ethyl acetate (5:3) as eluant to afford white crystals of the title macrocycle (207 mg, 26%), m.p. 42.0—43.5 °C; $\nu_{max.}$(KBr) 2 900, 1 565, 1 430, 1 275, 1 140, and 780 cm^{-1}; δ($CDCl_3$) 1.99 (4 H, quint, *J* 8 Hz, CCH_2C), 2.65 (4 H, t, *J* 8 Hz, CH_2SCH_2), 3.24 (4 H, t, *J* 8 Hz, CH_2Spyr), 3.68 (8 H, s, γ- and δ-CH_2O), 3.85 (4 H, t, *J* 6 Hz, β-CH_2O), 4.52 (4 H, t, *J* 6 Hz, α-CH_2O), 6.44 (2 H, d, *J* 8 Hz, β-pyrH), 6.76 (2 H, d, *J* 8 Hz, β-pyrH), and 7.36 (2 H, t, *J* 8 Hz, γ-pyrH); *m/z*, M^+ 526 (Found: C, 54.5; H, 6.5; N, 5.2. $C_{24}H_{34}N_2O_5S_3$ requires C, 54.7; H, 6.5; N, 5.3%).

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